Hardness Response of Different Composite Systems with Fine-Grained Nickel Electrodeposited Films

J. Lamovec[1, a], V. Jović[2, b], D. Trifunović[3, c], R. Aleksić[3, d], V. Radojević[3, e]

[1, 2]IChTM-Department of Microelectronic Technologies and Single Crystals, Njegoševa 12, 11000 Belgrade, Serbia

[3]Faculty of Technology and Metallurgy, Karnegijeva 4, University of Belgrade, 11000 Belgrade, Serbia

[a]jejal@nanosys.ihtm.bg.ac.yu, [b]vjovic@nanosys.ihtm.bg.ac.yu, [c]trifke@yubc.net, [d]aleksic@tmf.bg.ac.yu, [e]vesnar@tmf.bg.ac.yu

Keywords: Vickers microhardness; Ni electrodeposition; Composite hardness; Hardness models

Abstract. Thin Ni films have been electrodeposited from self-made sulphamate-based and commercially available sulphate-based electrolytes. DC electrodeposition was performed on polycrystalline cold-rolled Cu substrate and single crystal Si wafer with (100) orientation. In order to investigate the influence of the substrate and the microstructure of Ni electrodeposits on mechanical properties of these composite structures, Vickers microhardness testing for different loads were performed. Above a certain critical indentation depth, a measured hardness value is not the hardness of the electrodeposited film, but the so-called "composite hardness", because the substrate also participates in the plastic deformations during the indentation process. Critical indentation depth is influenced by the yield strengths ratio of the coating and the substrate. The yield strength ratio and critical indentation depth for these composite systems were calculated from Vickers microindentation test results. Composite hardness models of Chicot-Lesage and Korsunsky are applied to the experimental data in order to determine absolute film hardness.

Introduction

Thin films obtained with electrodeposition technology are often employed as components in microelectromechanical systems (MEMS). Electrodeposition is a simple, inexpensive, and versatile method to produce dense fine-grained films of many different metals or alloys. Electrodeposition is IC compatible as it is low-temperature and high rate deposition technology. Choice and optimization of the electrodeposition process parameters lead to ordered grain size and microstructure and because of that materials can be strengthened and hardened with little or no loss ductility.

Because electrodeposited thin films do not behave in the same manner as their bulk counterparts, there is a need for understanding and evaluation of mechanical material properties on a scale pertinent to MEMS. Good mechanical properties are critical for mechanical integrity of microsystems [1].

Electrodeposited Ni has good mechanical properties such as high yield strength and hardness. For MEMS devices a high electrical and thermal conductivity of Ni is also very important for some applications.

The indentation hardness test is commonly used to estimate the mechanical properties of coatings. The evaluation of the absolute hardness of thin films is difficult, because the influence of the substrate must be considered. The measured hardness varies continuously with the indentation depth, the film thickness and the hardness of the film and the substrate. The substrate starts to contribute to the measured hardness at indentation depths of the order of 0.07-0.20 times the coating thickness. Above a certain critical penetration depth, the measured hardness is called composite hardness and includes, except film hardness, also a component of the substrate hardness.

There is a need to obtain the hardness of the coating solely from the experimental composite hardness measurements and models of Korsunsky et al. [2,3] and Chicot and Lesage [4] .

Korsunsky and co-workers [2,3] have advanced a different approach to analyze hardness data for coated materials, employing dimensionless parameters. Model is applicable to either plasticity- or fracture- dominated behaviour, with all scales measured relative to the coating thickness. The approach is based on the assumption that the total work-of-indentation during a hardness test is composed of two parts: the plastic work of deformation in the substrate, W_S, and the deformation in the coating, W_F. The composite hardness H_C, according to this model, is given by:

$$H_C = H_S + \left[\frac{1}{1+k'\left(d^2/t\right)}\right]\left(H_F - H_S\right); \qquad k' = \frac{k}{49t}, \tag{1}$$

where k represents a dimensionless materials parameter related to the composite response mode to indentation, d is indentation diagonal, t is film thickness, H_S and H_F are substrate and film hardness respectively.

From Eq. (1) it is not possible to compute the film hardness at each indentation diagonal value since the magnitude of k should also be determined simultaneously from the experimental measurements of the composite hardness. This model does not allow computing the change in the film hardness with the indentation diagonal from the individual measurements of this property.

The model proposed by Chicot and Lesage (C-L) [4] avoids the knowledge or choice of any other data than that obtained easily from standard measurements (thickness and apparent hardness). Their model is based on the analogy between the variation of the Young modulus of reinforced composites in function of the volume fraction of particles [5], and that of the composite hardness.

Hardness value deduced from an indentation test is not constant because hardness is load-dependent. Meyer's law express the variation of the size of the indent in function of the applied load P. For the particular case of a film-substrate couple, the evolution of the measured diagonal and the applied load can be expressed by a similar relation as is Meyer's:

$$P = a^* d^{n^*}. \tag{2}$$

The variation part of the hardness number with load is represented by the factor n^*. Then they adopted the following expression:

$$f\left(\frac{t}{d}\right) = \left(\frac{t}{d}\right)^m = f \quad where \quad m = \frac{1}{n^*}. \tag{3}$$

The composite hardness can be expressed by the following relation:

$$H_C = \left(1-f\right)/\left(1/H_S + f\cdot\left(\frac{1}{H_F} - \frac{1}{H_S}\right)\right) + f\cdot\left(H_S + f\cdot\left(H_F - H_S\right)\right). \tag{4}$$

Hardness of the film is the positive root of the next equation:

$A\cdot H_F^2 + B\cdot H_F + C = 0$, with

$$A = f^2\cdot\left(f-1\right); B = \left(-2f^3 + 2f^2 - 1\right)\cdot H_S + \left(1-f\right)\cdot H_C; C = f\cdot H_C\cdot H_S + f^2\cdot\left(f-1\right)\cdot H_S^2 \tag{5}$$

The value of m (composite Meyer's index) is calculated by a linear regression performed on all the experimental points obtained for a given film substrate couple and deduced from the relation:

$$\ln d = m\cdot\ln P + b. \tag{6}$$

With the known value of m, only the hardness of the films remains to be calculated.

Experimental

The substrates for the electrodeposition were cold rolled polycrystalline Cu, chemically polished, and monocrystalline Si wafer with (100) orientation. The plating base for the silicon wafer were sputtered layers of 100 Å Cr and 1000 Å Ni. Electrodeposition was carried out using direct current galvanostate mode. Ni is deposited from two different electrolytes on the Cu substrates: self-made sulphamate bath consisting of 300 $g \cdot l^{-1}$ $Ni(NH_2SO_3)_2 \cdot 4H_2O$, 30 $g \cdot l^{-1}$ $NiCl_2 \cdot 6H_2O$, 30 $g \cdot l^{-1}$ H_3BO_3, 1 $g \cdot l^{-1}$ saccharine, and commercial sulphate bath, "Slotonik 20" ("Schloetter", Germany). Ni electrodeposition on Si wafers has been performed only from sulphamate electrolyte. The pH-value and the temperature of the process were maintained at 4.00 and 50 °C respectively. Deposition time was determined according with plating surface, projected thickness of deposit and cathodic current efficiency.

The mechanical properties of the composite systems were characterized using Vickers microhardness tester"Leitz, Kleinharteprufer DURIMET I" using up to 15 loads ranging from 4.9 N down to 0.049 N. Three indentations were made at each load, yielding six indentation diagonals measurements, from which the average hardness could be calculated. Indentation was done at room temperature. The experimental data were fitted with GnuPlot, v 4.0 (http://www.gnuplot.info/).

Results and discussion

Tests were performed with a Vickers diamond pyramidal indenter both on uncoated substrates and various coated substrates. Vickers microhardness indentation tests were carried out on Si monocrystalline substrate in such way that the indent diagonal was parallel with the prime flat, i.e. ⟨110⟩ direction on (100) oriented Si. It is well known that mechanical properties of single crystal Si depend on the crystallographic orientation [6] and this indenter orientation procedure was strictly applied during indentation.

The average values of impression diagonals (d in mm) were calculated from several independent measurements on every specimen for different applied loads, P (expressed in kgf). The composite hardness, H_c, in VHN (Vickers's hardness units), was calculated using the formula:

$$H_c = 1.8544\ P \cdot d^{-2}, \tag{7}$$

where 1.8544 is a constant, a geometrical factor for the Vickers pyramid.

At first, absolute hardness of substrates were determined.

According to literature [7], the PSR (Proportional Specimen Resistance) model of Li and Bradt is suitable for analysing load dependence hardness. The indentation test load P is related to indentation size d as follows:

$$P = a_1 d + (P_c / d_0^2) d^2. \tag{8}$$

Here P_c is the critical applied test load above which microhardness becomes load independent and d_0 is the corresponding diagonal length of the indent. A plot of P/d against d will give a straight line, and the slope gives the value of $P_c \cdot d_0^{-2}$ which when multiplied by the Vicker's conversion factor, 1.8544 from Eq. (7), gives the value of the load independent substrate microhardness, H_s. These calculated values of substrate microhardness's are 0.37 GPa for the polycrystalline Cu and 6.49 GPa for the (100) oriented Si substrate.

Hardness response of composite system consisting of hard coating on a soft substrate. Electrodeposited Ni on Cu substrate behaves as hard coating on soft substrate in this composite system.

Change of the composite hardness, H_c, with relative indentation depth $h \cdot t^{-1}$, where h is indent penetration depth and t is film thickness, for 10μm and 50μm-thick Ni films electrochemically deposited with different current densities (10 and 50 $mA \cdot cm^{-2}$) is shown on Fig. 1.

For shallow penetration depth ($h \cdot t^{-1} \leq 0.1$), the response is that of the film only, with little influence of substrate hardness. The composite hardness increases until certain relative indentation

depth (< 0.1), but then starts to decrease with indentation depth and growing influence of substrate. According to Kumar et al., [8], in the beginning of permanent deformation ($h \cdot t^{-1} < 0.1$), independent of the technique used to produce fine-grained nickel; a strong"work hardening" response is always observed. For penetration depth $h \cdot t^{-1} \sim 1$, the substrate hardness in the composite hardness value takes over dominant role.

Change in the composite hardness H_c with indentation diagonal d, for 10 μm thick Ni films obtained from different electroplating baths is shown on Fig. 2. Experimental data are described by Korsunsky et al. model. According to our earlier investigations, this model provides the best fit to experimental data [9].

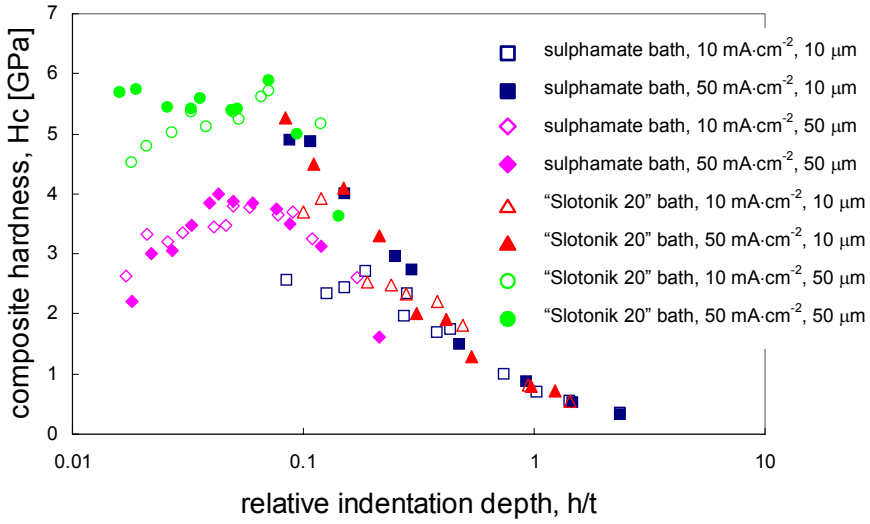

Fig. 1. Composite hardness dependance on the relative indentation depth for electrodeposited Ni films on Cu substrate. Film thickness, current densities and baths are given on the diagram.

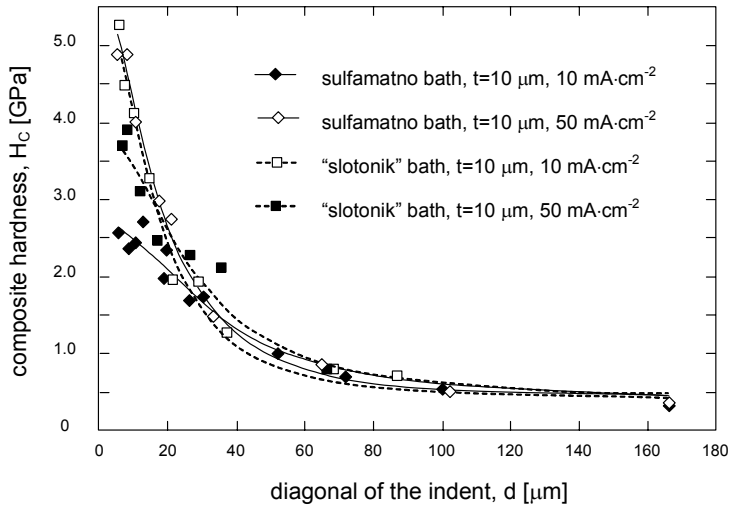

Fig. 2. Experimental values of composite hardness, H_c, as a function of the indent diagonal lenght, d, for electrodeposited Ni films on a copper substrate. Ni films of 10μm thickness are electrodeposited from two different electrolytes with two values of current densities. Experimental data are fitted with Korsunsky et al. model

Hardness response of composite system consisting of soft coating on a hard substrate. In Table 1. are given curve-fit data of absolute hardness of the film H_F and coefficient k' from the Korsunsky model (Eq. 1) for four electrodeposited Ni films on Cu substrates. Standard fitting error, given in the same table, also points towards Korsunsky model as one which is the best for describing composite hardness of this hard film-soft substrate system.

Change of the composite hardness *Hc* with relative indentation depth *h/t*, for electrodeposited Ni films of different thickness ranging from 2 to 50 μm on Si (100) oriented substrate is shown on the Fig. 3. Ni films are obtained with two current densities: 10 mA·cm^{-2} or 50 mA·cm^{-2}, which is notified on the diagram.

The microhardness values of the electrodeposited Ni layers are influenced by the current density. Increase in current density leads to decrease in grain size and results in higher values of the microhardness. Composite hardness model of Korsunsky et al. does not fit experimental data for this composite system of soft coating on hard substrate well [9]. Model of Chicot and Lesage, based on the model for reinforced composites [4] can be applied to experimental data of given system.

Table 1. Values of the fitting results for Ni film hardness according to the Korsunsky et al. model. Last column in table shows standard fitting error for H_F and k from Eq. 1

sulphamate bath, t = 10 μm, 10 mA·cm^{-2}	H_F	2.68	$\pm 1.1 \cdot 10^{-1}$ (4.1%)
	k'	0.0087	$\pm 1.7 \cdot 10^{-3}$ (20%)
sulphamate bath, t = 10 μm, 50 mA·cm^{-2}	H_F	5.40	$\pm 1.2 \cdot 10^{-1}$ (4.1%)
	k'	0.0290	$\pm 2.0 \cdot 10^{-3}$ (8.2%)
Slotonik 20 bath, t = 10 μm, 10 mA c·cm^{-2}	H_F	3.88	$\pm 2.5 \cdot 10^{-1}$ (6.6%)
	k'	0.013	$\pm 3.8 \cdot 10^{-3}$ (27.7%)
"Slotonik 20" bath t = 10 μm, 50 mA·cm^{-2}	H_F	5.69	$\pm 2.5 \cdot 10^{-1}$ (4.4%)
	k'	0.038	$\pm 5.7 \cdot 10^{-3}$ (15%)

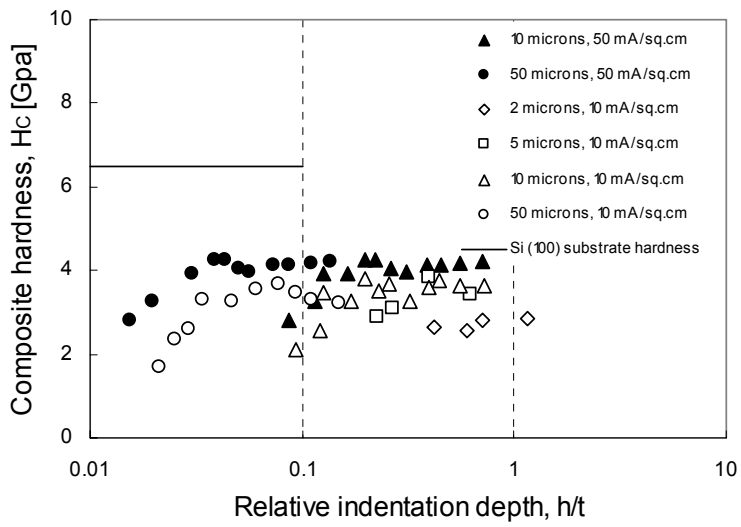

Fig. 3. Dependence of composite hardness, H_C, on relative indentation depth, $h \cdot t^{-1}$, for a film of electrodeposited Ni on a (100) oriented Si. This is the case of soft film on hard substrate. Ni films are electrodeposited from sulphamate bath

On Fig. 4. mentioned model, i.e. C-L, is applied on Ni film with different thickness as indicated on the graph. Films are obtained with two current densities from sulphamate electroplating bath.

The values obtained for the film hardness H_F, are not constant but influenced by the applied load.

Different physical phenomena such as indentation size effect, cracking of the film around the indent or the elastic contribution of the substrate for the lowest loads, may be the reasons for the film hardness variations. The composite system Ni film-Si substrate shows decreasing manner dependence of film hardness on relative indentation depth.

According to two-dimensional model of plastic deformation during indentation [10], the approximate determination of the yield strength, *Y*, of substrates and films is possible from the microhardness testing as:

$$H = 3 \cdot Y \tag{9}$$

For the substrates of Cu and (100) oriented Si the yield strength values are Y_{Cu} = 0.12 GPa and $Y_{Si(100)}$ = 2.16 GPa. The yield strength for the Ni films from sulphamate bath is about 0.89 GPa. Both of our systems (Ni-Cu substrate and Ni-Si substrate), have $Y_F / Y_S < 10$, and therefore the

substrates were involved in the composite hardness earlier than relative indentation depth reaches the value $h \cdot t^{-1} = 0.1$ (known as "one-tenth rule").

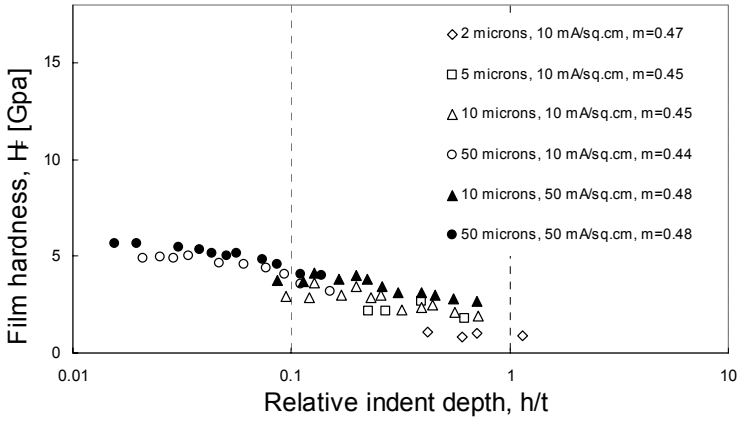

Fig. 4. Variations in film hardness with relative depths for the system which consists of electrodeposited Ni film on (100) oriented Si substrate according to C-L model. Ni films were electrodepolsited from sulphamate electrolyte bath.

Conclusion

Hardness of nickel films electrodeposited on substrates of polycrystalline cold rolled Cu and single crystal Si with (100) orientation was investigated. Electroplating was carried out in DC mode, from self-made sulphamate and commercial sulphate "Slotonik 20" baths, under the chosen plating conditions of pH = 4.00 and t = 50 °C. The current density values were maintained at 10 or 50 $mA \cdot cm^{-2}$, which resulted in different microstructures and thus in film's mechanical properties.

Ni film on Cu substrate represents the composite system of "hard film on a soft substrate". Ni films obtained from commercial sulphate bath are harder than the films from the sulphamate-based electrolyte, because certain additives are added at commercial bath. In the composite region ($0.1 < h \cdot t^{-1} < 1$), the substrate is involved in the composite hardness value and the hardness difference decreases. Films obtained with higher current density have higher values of composite and film hardness. Korsunsky et al. model gives the best fit of data for the system Ni film-Cu substrate.

Nickel films on Si substrate can be thought as "soft film on a hard substrate" system. Model Chicot-Lesage for reinforced composites was chosen for this system description and the film hardness was calculated for every indentation diagonal. The film hardness decreases with increasing relative indentation depth, i.e. toward the substrate region.

Approximately calculated, shown systems (Ni-Cu and Ni-Si), have $Y_F/Y_S < 10$, and therefore the substrates were involved in the composite hardness earlier than relative indentation depth reaches the value $h \cdot t^{-1} = 0.1$ (known as"one-tenth rule").

References

[1] M. Datta, D. Landolt: "Fundamental aspects and applications of electrochemical microfabrication", Electrochimica Acta, Vol. 45 (2000) p. 2535.
[2] A.M. Korsunsky, M.R. McGurk, S.J. Bull, T.F. Page: Surf. Coat. Technol., Vol. 99 (1998) p. 171.
[3] J. R. Tuck, A. M. Korsunsky, D.G. Bhat, S. J. Bull: Surf. Coat.Technol., Vol. 137 (2001) p. 217.
[4] J. Lesage, A. Pertuz, E.S. Puchi-Cabrera, D. Chicot: Thin Solid Films, Vol. 497 (2006) p. 232.
[5] W. D. Callister Jr.: *Materials Science and Engineering, An introduction*, Fidth Edition, John Wiley & Sons, Inc. (1999) p. 523.
[6] S. Mukerji, T. Kar: Cryst. Res. Technol., Vol. 34 (1999) p. 1323.
[7] H. Li and R.C. Bradt: Mater. Sci. Eng. A, Vol. 142 (1991) p. 51.
[8] K.S. Kumar, S. Suresh,M.F. Chisholm, J. Horton, P. Wang: ActaMaterialia, Vol. 51 (2003) p. 387.
[9] J. Lamovec, V. Jovic, D. Trifunovic, R. Aleksic, V. Radojevic: Balkan Conference on Metallurgy, 2006., Proceedings
[10] D. Lebouvier, P. Gilormini, E. Felder: J .Phys. D: Appl.Phys. 18(1985)199.